A New Selective Membrane Electrode for Oxalate Based on N,N'-Bis(salicylidene)-2,2-dimethylpropane-1,3-diamine Ni(II)

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A new solvent polymeric membrane electrode, based on N,N'-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine Ni(II) as the ionophore, was designed. The oxalate-selective electrode has the dynamic range between 1.0×10^{-6} M and 1.0×10^{-1} M with a Nernstian slope of -28.7 ± 1.0 mV per decade. The detection limit was 6.3×10^{-7} M. The proposed electrode revealed good selectivities for oxalate over a variety of other anions and could be used in a pH range of 2.0-7.8. The electrode can be used for at least two months without any considerable divergence in potential. The designed electrode was applied as an indicator electrode in the potentiometric determination of oxalate in real samples.

Key Words : Ion-selective electrode, Oxalate, Potentiometry, Membrane

Introduction

Ion Selective electrodes (ISEs) have found widespread uses, especially, for the direct determination of ionic species in whole and diluted blood, serum, urine, tissue and intracellular samples.[1] The most attractive features of this technique are the speed with which samples can be analyzed, portability of the device, samples are not destroyed, online monitoring, cost effectiveness and large measuring range.[2] One of the most important figures of merit for an anion ISEs is its selectivity towards a specific analyte, which is generally limited by the interaction of the ionophore within the membrane with other ions. The selectivity of anion ISEs is generally governed by specific and non-specific interactions. Specific interactions are based on chemical recognition principle, where a recognition element such as the metal-ligand interaction is used to achieve the required selectivity. Non-specific interactions, which are generally governed by the so-called Hofmeister pattern, are based on both lipophilicity and electrostatic interactions. Therefore, these interactions are essentially "non-selective".[3]

Recently, the study of anti-Hofmeister sensing materials with the high selectivity of the given anions is an expanding scope. Researching on anti-Hofmeister sensing materials is an expeditiously expanding domain in chemical sensors. Recently ion selective electrodes, using plasticized polyvinyl chloride (PVC) membranes doped with organometallic species and a metal-ligand complex including organomercury derivatives of vitamin B_{12}, Mn(IV), Co(III), Sn(IV), Porphyrine complexes and so on displayed potentiomertic anion-selectivity sequences, which observably deviated from the classical Hofmeister pattern.[4-9]

Oxalate is one of the important nutrients in the human diet found principally in spinach, beet leaves, etc. Oxalate is primary chelator of calcium ion, so it forms chelates with dietary calcium, thus gives the complex unavailable for adsorption in the body and absorbed oxalate is also precipitated as insoluble salts that accumulate in the renal tissue. So, calcium oxalate is a most important phase in case of stone diseases.[10] Determination of oxalate in different food matrices is of great interest because a high oxalate level in the foodstuff may cause the formation of insoluble kidney stones as a result of unbalanced nutritional habits. The measurement of oxalate in urine is important in the diagnosis of hereditary and enteric hyper-oxalauria and in the evaluation and management of patients with urinary calculi (stones). Calculi are deposited chemicals in compact form and these concretions are frequently found in urinary tract. Therefore, the determination of oxalate in the some biological material is important. Several determination methods of oxalate, such as; spectrophotometric,[11] amperometric,[12-15] spectrofluorimetric,[16] chemiluminescence[17] and ion selective electrode method[18,19] have been proposed. However, those methods are not sufficiently sensitive. Other methods such as; isotope dilution mass spectrometry,[20] differential pulse polarography[21] and chromatography[22-24] are also used for oxalate determination but these methods require special instrumentation and relatively high cost of analysis. So, a simple, sensitive and inexpensive determination method of oxalate is required. In this study, the construction and evaluation of a novel ion-selective electrode, with high selectivity toward oxalate based on PVC membrane of a compound N,N'-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine Ni(II) is described.

Experimental Section

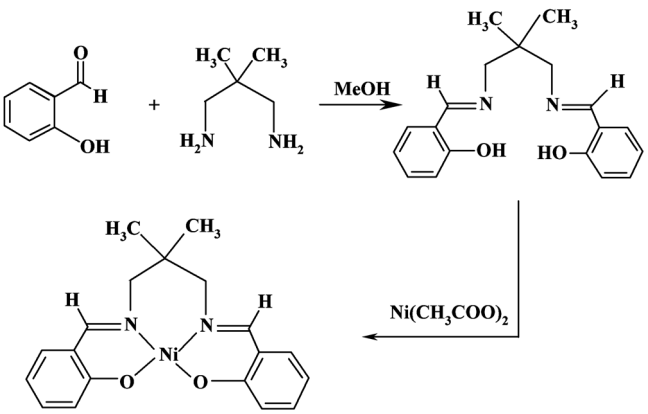
Reagents. PVC of high relative molecular weight, trioctyl methylammonium chloride (TOMAC), dibutyl phthalate (DBP), dibutyl sebasate (DBS), dioctyl phthalate (DOP),

sodium tetraphenylborate (NaTPB) were obtained from Merck and other chemicals were of the highest purity available from Merck and were used without further purification, except THF, which was distilled before use. All aqueous solutions were prepared with deionized, distilled water. The ionophore was prepared as follows: a stock solution of 1.0×10^{-1} M sodium oxalate was prepared by dissolving 8.005 g of sodium oxalate in 100 mL of water. Solution of anionic interferences, for selectivity studies, was prepared mostly from sodium salts in the water. Working solutions were prepared by successive dilutions with water.

Synthesis of ionophore.

Preparation of [Ni(salpnMe$_2$)]: To a solution of 2.44 g of salicylaldehyde (0.02 mol) in 25 mL of methanol, 1.02 g 2,2-dimethylpropane-1,3-diamine solution (0.01 mol) was added over a period of 1 h. The mixture was refluxed for 4 h in a water bath. After the solution was concentrated, the yellow precipitate "(N,N'-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine; H_2 [salpnMe$_2$]" was washed with methanol and dried over $CaCl_2$ in vacuum (Yield: 84%). Anal. calcd for H_2 [salpnMe$_2$]: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.14; H, 6.96; N, 8.81%. ^{1}H-NMR (400 MHz) chemical shift 15.17 (s, 2H, OH), 7.47 (s, 2H, -CH=N-), 6.51-7.26 (m, 8H, aromatic), 4.37 (s, 4H, CH_2) and 1.17 ppm (s, 6H, CH_3-C-). Selective IR bands (cm^{-1}), KBr pellets, (C=N), 1590 cm^{-1}.

The flask, containing a stirred suspension of nickel (II) acetate tetrahydrate (3.98 g, 0.016 mol) in propanol (100 mL) was purged with nitrogen and then warmed to 50 ºC under a nitrogen atmosphere. N,N'-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine (5.41 g, 0.016 mol) was added in one portion and the resulting suspension was then stirred and refluxed under the nitrogen atmosphere for 8 h. Then the mixture was cooled and filtered under the reduced pressure. The collected solid was washed with diethyl ether and dried in air to give a red crystalline [Ni (salpnMe$_2$)] (NiL, Scheme 1), which was purified by re-crystallization from chloroform (Yield: 61%). Anal. calcd for [Ni (salpnMe$_2$)]: C, 62.12; H, 5.49; N, 7.63, Ni, 16.00. Found: C, 62.03; H, 5.33; N, 7.48; Ni, 15.82%. Selective IR bands (cm^{-1}), KBr pellets, (C=N, Ni-N, Ni-O), 1551, 448, 514 cm^{-1}. dd (in chloroform solutions at 25 ºC as never specified), 24250 cm^{-1}.



Scheme 1

Electrode preparation: The membrane ion-selective electrodes were prepared according to a previously reported method.[25] A mixture of PVC, plasticizer (DOP) and the membrane additive (TOMAC) with a total mass of 200 mg was dissolved in approximately 10 mL freshly distilled THF. To this mixture was added the electroactive material [NiL] and the solution was mixed well. The resulting mixture was poured into a small flat bottom dish of 2 cm diameter, covered with a filter paper and the solvent was allowed to evaporate at room temperature until an oily mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 10 s so that a non-transparent membrane, 0.3 mm thickness, was formed. Then, the tube was then pulled out from the mixture and kept at the room temperature for 1 h. The tube, with the membrane, was then incorporated into an Ag/AgCl wire electrode (an internal reference electrode). The electrode was then filled with an internal solution of 1.0×10^{-3} M oxalate. The prepared electrodes were finally conditioned by soaking in a 1.0×10^{-3} M oxalate solution for 12 h.

Apparatus

Measurements of potentials: The electromotive force (emf) values were detected to the nearest value of 0.1 mV with a pH/mV meter "Metrohm" model 691. All the measurements were preformed at ambient temperature (25 ± 1 ºC), using a pH/mV meter. The performance of each electrode was investigated by measuring its potential in the solutions, prepared with the concentration range of 1.0×10^{-7}-1.0 M by serial dilution at a constant pH. The pH of the sample solution was monitored simultaneously with a conventional glass pH electrode (Metrohm). The electrochemical system for this electrode can be represented as follows:

Ag|AgCl| internal solution (KCl 3.0 M, [Oxal^{2-}] 1×10^{-3}M)| PVC membrane| test solution ¦¦ SCE

Activities were calculated according to the Deby-Hückle procedure.[26] The calibration curve was also constructed by plotting the concentration of oxalate instead of activity. The solutions were stirred and potential readings were recorded when they reached the steady state values. The data were plotted as observed potential against the logarithm of the oxalate concentration. Potentiometric selectivity ($K_{Oxalate, A-}$) were determined by the fixed interference method (FIM). A UV-Visible spectrophotometer (GBC, spectrophotometer) was used for recording the absorbance spectra.

Results and Discussion

Response of the electrode to various anions. In the preliminary experiments, the potentiometric responses for various anions were investigated with the membrane electrode, based on [NiL], in a PVC matrix without any amount of additive. It should be noted that ionic additives are ion exchangers, which themselves induce a selective response if no or only an insufficient amount of ionophore is present. In this case, all the electrodes were conditioned in 1.0×10^{-3} M

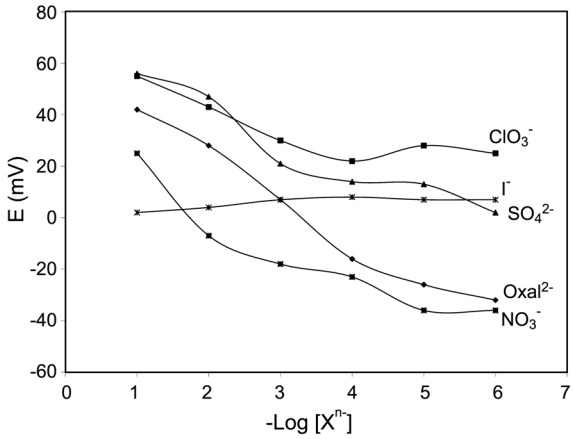


Figure 1. Plot of response of anions (nitrate, sulfate, iodide, and chlorate) to N,N'-2,2-dimethylpropane-1,3-diamine Ni(II) used as ionophore. Each electrode was conditioned in a 1.0 × 10^{-3} M solution of the corresponding anion for 24 h.

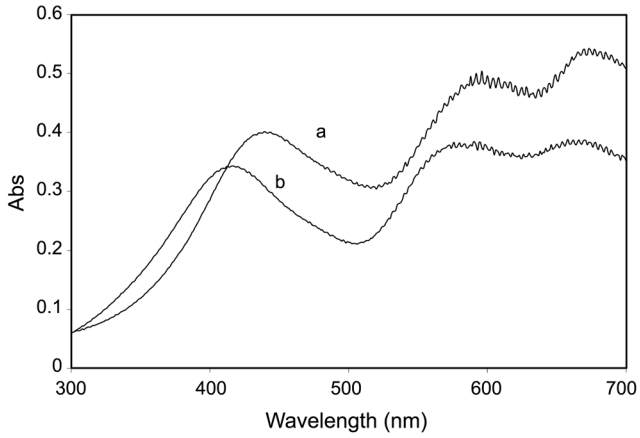


Figure 2. UV/vis spectrum of 5.0 × 10^{-4} M N,N'-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine Ni(II) in (a) THF and (b) after 1 h treatment with 1.0 × 10^{-3} M Oxalate solution.

solution of the corresponding anion. As it is obvious from the Figure 1 that with the exception of oxalate ion, all the tested anions showed negligible responses in the concentration range of 1.0 × 10^{-6} - 1.0 × 10^{-1} M, due to their very weak interactions with ionophore. This is, most probably, due to the specific interaction between oxalate and [NiL]. The electrode, based on NiL, exhibits an excellent performance as an anion sensor for oxalate ion with a Nernstian response to the concentration of oxalate in the range of 1.0 × 10^{-6} - 1.0 × 10^{-1} M. In order to investigate the interaction between the ionophore [NiL] and oxalate, UV-spectrum was obtained. UV-visible spectrum of a THF solution of [NiL] and [NiL]-treated with sodium oxalate is shown in Figure 2, which shows that the wavelength maximum (λ_{max}) shifted to the lower wavelengths following the addition of oxalate ion. The substantial decrease in the absorbance and wavelength after the contact of carrier solution with the oxalate suggests the occurrence of a specific interaction between the ionophore and the anion in the solution. During the same method, the effects of other anions on the spectrum of the carrier were investigated. No detectable changes in the UV/vis spectra were observed. Thus we optimized the ingredients of the membrane to obtain the best potentiometric characteristics toward the oxalate ion.

Optimization of the amount of compositions in the membrane electrode. It is well known that the sensitivity, linearity and selectivity, obtained for a given ionophore, depends significantly on the membrane composition, nature and the amount of additive used.[2,27-31] The percentage of membrane solvent in poly (vinyl chloride) membranes and the membrane solutions for micro-electrodes is very high (60-90 wt.%). Hence, the membrane solvent has to exhibit excellent plasticizer properties for use in solvent polymeric membranes. The high concentration of the membrane solvent substantially affects a number of parameters, which influence the membrane electrode properties. The choice of an appropriate membrane solvent is governed by several criteria, such as chemical stability, chemical inertness, adequate dielectric constant, high lipophilicity, etc. Thus, the influence of the amount of ionophore, plasticizers and lipophilic additives on the potential response of the sensor was investigated, and the results are summarized in Table 1. The influence of plasticizer type on the response characteristics of the oxalate electrodes was investigated by using different plasticizers including DBP and DOP. In all cases, the plasticizer/PVC mass ratio of 2 resulted in highest sensitivity. Among the several membranes, the membranes

Table 1. Evaluation of different membrane composition of oxalate-selective electrode

No:	PVC%	Plasticizer %	Ionophore%	Additive%	Slope (mVdecade^{-1})	Linear Range (M)
1	32	64 (DOP)	4	0	–19	1.0 ×10^{-1} - 1.0 ×10^{-4}
2	32	64(DBP)	4	0	–17	1.0 ×10^{-2} - 1.0 ×10^{-5}
3	33	64 (DOP)	2.5	0.5 (TOMACl)	–20.21	1.0 ×10^{-1} - 1.0 ×10^{-4}
4	31.5	63.5(DOP)	4.5	0.5 "	–26.3	1.0 ×10^{-1} - 1.0 ×10^{-5}
5	31	63 (DOP)	5	1 "	–28.71	1.0 ×10^{-1} - 1.0 ×10^{-6}
6	30	63(DOP)	6	1 "	–24.4	1.0 ×10^{-2} - 1.0 ×10^{-5}
7	31	61 (DOP)	6	2 "	–26.6	1.0 ×10^{-2} - 1.0 ×10^{-6}
8	31	61(DOP)	7	1 "	–25.7	1.0 ×10^{-2} - 1.0 ×10^{-5}
9	27	67(DOP)	5	1 "	–24.4	1.0 ×10^{-2} - 1.0 ×10^{-6}
10	31	63 (DBP)	5	1 "	–23.1	1.0 ×10^{-2} - 1.0 ×10^{-5}
11	31	63(DOP)	5	1 NaTPB	–19	1.0 ×10^{-2} - 1.0 ×10^{-4}

incorporating DOP generally showed better potentiometric responses, *i.e*; higher sensitivity and wider linearity of the calibration plots. It seems that DOP, as a low polarity and a relatively high mobility, with respect to other plasticizer examined, provides appropriate conditions for incorporation of lipophilic oxalate ion into the membrane. The performance of most ion-selective carrier membranes can be improved by membrane additives. It has been shown that the incorporation of lipophilic anionic or cationic additives can significantly change the selectivity of anion selective electrodes. The properties of ion-selective electrode based o electrically charged and neutral ionophores are strongly influenced by the ionic sites in their membranes. Since the widely used uncharged carriers are neutral when uncomplexed and the complexes have the same charge the analyte ion, the respective membranes require the additional incorporation of lipophilic ions of opposite charge to obtain a Nernstian response, a decrease in the membrane resistance, a reduction in co-ion interferences, and an improvement in the detection limit and optimization of the selectivity. The influence of the type and concentration of the membrane additives were investigated by incorporating TOMAC or NaTPB into the membranes. The potentiometric sensitivity of the membranes, based on [NiL], was greatly improved in the presence of TOMAC as a lipophilic cationic additive, compared to the membranes with no additive at all. No anionic response was observed when the anionic additive, NaTPB, was incorporated. Previous studies have shown that there is an optimal concentration of lipophilic ionic additives in the membranes that gives the best electrode performance. The effect of TOMAC concentration in the membranes was investigated at several carrier/additive mole ratios. Better response characteristics, *i.e*; Nernstian response and improved selectivity, were usually observed with an ionophore/TOMAC weight ratio of approximately 5.0, which corresponds to a mole ratio of approximately 5.7. The response of the blank membranes, containing additives but no carrier at all, was far from Nernstian. Irrespective of ionophore concentration, the slope was relatively larger when DOP/PVC weight ratio was approximately 2.0. Results have shown which of the plasticizer/PVC ratios of *ca*. 2 produced maximum sensitivity.[32]

It is seen from Table 1 that among different membrane compositions tested, the membrane No. 5, with 5% [NiL], 31% PVC, 63% DOP and 1% TOMAC, offers the widest linear range with a Nernstian slop of −28.7 ± 1.0 mV per decade. Over the concentration range of 1.0×10^{-6}-1.0×10^{-1} M of oxalate in the calibration solution, the electrode potential response was linear with the concentration of oxalate. The calibration curve slope was −28.7 ± 1.0 mV/p [oxalate] and the detection limit, calculated as recommended by the IUPAC[33,34] was 6.3×10^{-7} M. The calibration plot is shown in Figure 3, which shows the linear range from 1.0×10^{-6}-1.0×10^{-1} M; the Nernstian slope is −28.7 ± 1.0 mV decade^{-1} of oxalate concentration.

The potentiometric response of the prepared oxalate-selective electrode was investigated against the oxalate ion concentration. For this purpose, appropriate aliquots of a stock solution of oxalate were introduced to the cell and the corresponding potentials were determined. The potential readings were plotted against -log of the oxalate concentration. The characteristic properties of the optimized membrane are summarized in Table 2.

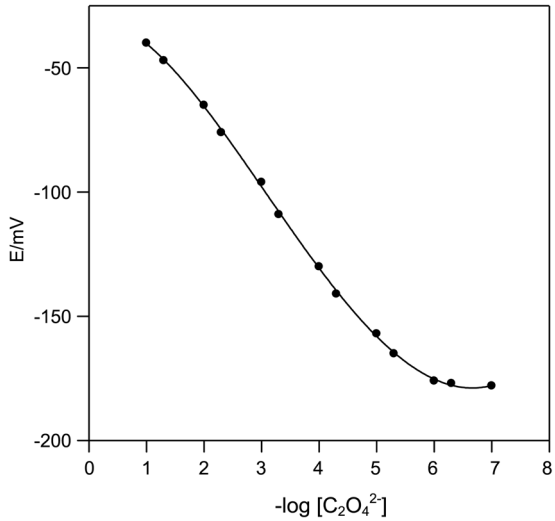


Figure 3. Potentiometric response of the oxalate-selective electrode based on N,N'-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine Ni(II) towards oxalate anion.

Optimization of pH. The pH dependence of the membrane electrode was tested over the pH range of 2-11 at an oxalate concentration of 1.0×10^{-3} M and the results are shown in Figure 4. The results show that the sensor is suitable for oxalate determination with the wide pH range of 2.0-7.8. In high pH media, probably OH^- will compete with oxalate ion, whereas in acidic media (pH < 2.0), the drift in the potential may be due to the instability of the ionophore due to the nitrogen sites protonation (or formation of oxalic acid). The working pH range, over which the electrode can be used (2.0-7.8), covers the physiological conditions (pH 7.2-7.6). However, in highly alkaline media, the potential increases.

Response characteristics of oxalate-selective electrode. The influence of the concentration of the internal solution on

Table 2. Characteristics of optimized oxalate-ISE

Linear range / M	1.0×10^{-6} - 1.0×10^{-1} M
Slope / mVdecade^{-1}	−28.7
pH range	2.0-7.8
Standard deviation of slope (mVdecade^{-1})	± 1.0
Precision	At concentrations of 1.0×10^{-3} M and 1.0×10^{-4} M oxalate standard deviations were of ± 0.7 mVand ± 0.9 mV respectively.
Detection limit/M	6.3×10^{-7}
Life time/month	> 2
Response time/s	5-15

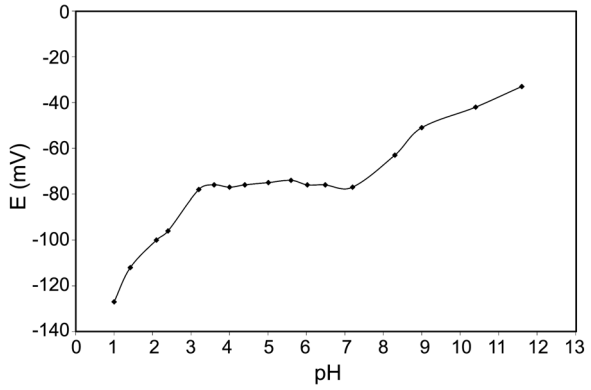


Figure 4. The influence of pH on the potential response of the optimized Oxa-ISE for a) 1.0×10^{-3} M oxalate concentration.

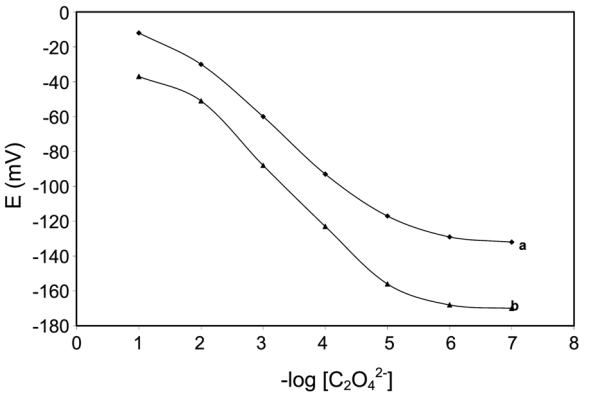


Figure 5. The influence of the concentration of internal solution on the potential response of the optimized Oxa-ISE: (a) 1.0×10^{-2} M, (b) 1.0×10^{-3} M.

the potential response of the polymeric membrane electrode was also studied. Thus, two similar membranes were prepared under optimal membrane composition and each electrode was filled with an internal solution of varying oxalate concentration (1.0×10^{-2} and 1.0×10^{-3} M). Then, the electrodes were conditioned by soaking in the same solutions of oxalate. Finally, plot of the emf oxalate selective electrode versus p[oxalate] was investigated for each electrode. The results are shown in Figure 5, which shows that the concentration of the internally filled solution has a neglible effect on the potential response of the electrode, except for the expected plots, which showed that the variation in the concentration of the internal solution changes the linear range and intercept of the resulting plots. Thus, based on the results, the concentration of 1.0×10^{-3} M was selected for further studies.

To evaluate the reproducibility of emf response of the cell assembly, alternating measurements were performed in 1.0×10^{-3} and 1.0×10^{-4} M of oxalate solution. The procedure was repeated 20 times and the results are given in Table 2.

The response time of electrochemical cells, containing ion-selective membrane electrodes, is considered to be one of the most critical and limiting factors in the chemical and biochemical applications of potentiometric sensors. Since, the composition of the membranes in ion-selective electrodes remains approximately constant; the diffusion processes of ions passing through the membrane become negligible in the absence of interfering ions. As a result, the dynamic response characteristic is governed by the transport processes in the aqueous diffusion layer, *i.e*; the response time depends on the shape and condition of the membrane surface as well as the compositin of the sample. Furthermore, it is markedably influenced by the direction of the change in activity in the sample solution. Also, the response time of membrane selective electrodes, containing lipophilic salts, can be reduced by minimizing the aqueous diffusion layer (fast stirring, flowing the sample and micro-electrodes) and by using samples of higher activities. The t_{90} response time, as recommended by IUPAC, was used (where t_{90} is the time required for the electrode to reach 90% of the steady-state value). Under these conditions, t_{90} was found to 5-15 s for all the ranges of oxalate concentration. The response time of the electrode increases when concentration of oxalate is lowered, as illustrated in Figure 6. This is caused by the increased thickness of the diffusion layer near the membrane of electrode.[35]

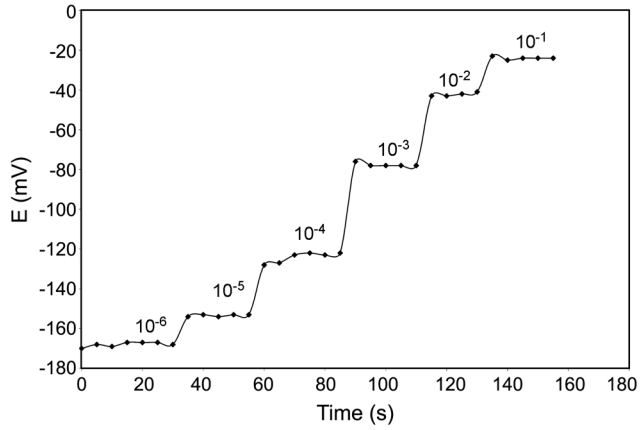


Figure 6. Response time of the optimized Oxa-ISE for stepwise changes in the concentration of oxalate: a) 1.0×10^{-6} M, b) 1.0×10^{-5} M, c) 1.0×10^{-4} M, d) 1.0×10^{-3} M, e) 1.0×10^{-2} M and f) 1.0×10^{-1} M.

The life time of an ion-selective measuring system may be defined as the time interval between the conditioning of the membrane and the moment when at least one parameter of the functionality characteristics of the device changes detrimentally. For ion-selective membrane electrodes, the life time is mainly limited to the following two processes:[36] a) The first process is the leaching out of carrier molecules from the membrane phase to the sample as an effect of a low partition coefficient at the sample/membrane interface. b) The second process is the extraction of the plasticizer by the sample and/or the degradation of the mobile ionic site additives of the membrane phase, which may catalyze the ion transfer. The electrode could be used for two months, without any measurable change in potential. During this time, the detection limit and slope of electrode remained almost constant.

Selectivity and interferences. Selectivity behavior is obviously one of the most important characteristics of an

Table 3. Selectivity of coefficients, determined by use of the matched potential method (MPM) for the oxalate-selective electrode

Interfering Ion	$\log K^{pot}_{oxa,A^-}$	Interfering Ion	$\log K^{pot}_{oxa,A^-}$
F^-	–4.6	N_3^-	–2.8
Cl^-	–3.6	Citrate	–4.9
Br^-	–3.8	HCO_3^-	–4.9
I^-	–3.7	SO_3^{2-}	–3.8
CN^-	–3.9	ClO_4^-	–2.2
SCN^-	–2.6	NO_2^-	–4.1
CO_3^{2-}	–3.0	SO_4^{2-}	–2.3
OAc^-	–2.4	NO_3^-	–3.8

ion-selective electrode, which is the relative electrode-response for the primary ion over other ions present in the solution. The selectivity of the membrane electrode is governed by both the mobility of the ions in the membrane and the equilibrium that exists at the membrane solution interfaces (*e.g.* partition coefficients, ion exchange equilibrium constants). In this work, the potential response of the proposed oxalate ion selective sensor to other anions was investigated by the matched potential method (MPM).[37-39] This is a recently recommended method by IUPAC,[38] which gets rid of the limitations of the corresponding methods based on Nicolsky-Eisenman equation for the determination of potentiometric selectivity coefficients (including the fixed interference and the mixed solution methods).[40] These limitations include non-Nerstian behavior of interfering ions and in equality. According to the MPM, a special activity (concentration) of the primary ions (A) is added to a reference solution, and the potential is measured. In a separate experiment, interfering ions (B) were successively added to an identical reference solution until the measured potential matched the one obtained before by adding primary ions. The MPM selectivity coefficients, $K_{Oxa,\,B}$, are thus given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K_{Oxa,\,B} = a_{Oxa}/a_B$.

The resulting values thus obtained for the proposed oxalate selective electrode are summarized in Table 3. As seen, most of the diversely used anions cannot significantly disturb the functioning of the oxalate selective membrane electrode. It is interesting to note that the observed selectivity pattern:

$C_2O_4^{2-} > ClO_4^- > SO_4^{2-} >$ Acetate $> SCN^- > N_3^- > CO_3^{2-} > Cl^- > I^- > Br^- = NO_3^- = SO_3^{2-} > NO_2^- > F^- > HCO_3^- =$ Citrate

The sequence is characterized by the Hofmeister series: $R^- > ClO_4^- > SCN^- > I^- > NO_3^- > Cl^- > HCO_3^- > SO_4^{2-} > HPO_4^{2-}$

Selectivity pattern of the proposed electrode considerably differs from the so-called Hofmeister selectivity sequence (*i.e*; selectivity based solely on lipophilisity of the anions).[41] The reason that the selectivity coefficients of this electrode do not comply with the Hofmeister series, and show an anti-Hofmeister behavior, is thought to be due to the possible interaction of the anions with copper.

In Table 4, the response characteristics of the proposed electrode are compared with those of the three recently reported selective electrodes for $C_2O_4^{2-}$ ion.[18,19] The linear range and the selectivity coefficients of the proposed electrode are superior to those of other electrodes reported in the literature, in all cases (Table 4).

Analytical applications. The high degree of oxalate selectivity exhibited by the electrode, based on N,N'-bis (salicylidene)-2,2-dimethylpropane-1,3-diamine Ni(II) as a carrier, makes it to be potentially useful for monitoring concentration levels of oxalate in water samples. In order to assess the applicability of the membrane electrode, an attempt was made to determine $C_2O_4^{2-}$ in several water samples using the standard addition method. The proposed electrode was employed to determine the recovery of oxalate ions of water sample and interfering effect of other anions

Table 5. Determination of oxalate in water samples by Oxa-ISE

Sample No.	Initial (Oxalate added (M))	Found [Oxa-ISE (M)[a]]
1	1.21×10^{-5}	$1.13(\pm 0.56) \times 10^{-5}$
2	2.38×10^{-5}	$2.23(\pm 0.56) \times 10^{-5}$
3	3.48×10^{-5}	$3.28(\pm 0.56) \times 10^{-5}$

Table 6. Determination of oxalate in synthesis samples by Oxa-ISE

Concentration of different anions	Oxalate added (M)	Oxa-ISE (M)[a]
NO^{3-} (1.0×10^{-4} M) CO_3^{2-} (1.0×10^{-4} M) SCN^- (1.0×10^{-4} M)	1.0×10^{-2}	$1.11(\pm 0.20) \times 10^{-2}$
SO_3^{2-} (1.0×10^{-3} M) Cl^- (1.0×10^{-3} M) ClO_4^{2-} (1.0×10^{-3} M)	1.0×10^{-2}	$1.22(\pm 0.10) \times 10^{-2}$

[a]TMean value ± standard deviation (n = 5).

Table 4. Comparison of the potentiometric parameters of the proposed Oxalate-selective electrode with the three oxalate-selective electrodes

A^-	The proposed oxa-ISE	Ref:18[a]	Ref::18[a]	Ref: 19
Nernstian slope, mV/decade (Mean value ± standard deviation)	–28.7 ± 1.0	–25.6 ± 0.1	–23.6 ± 0.1	–29.2 ± 0.6
Linear range, M	1.0×10^{-6} - 1.0×10^{-1}	1.0×10^{-8} - 1.0×10^{-4}	1.0×10^{-7} - 1.0×10^{-4}	5.0×10^{-8} - 1.0×10^{-1}
Limit of detection, M	3.0×10^{-7}	1.0×10^{-9}	1.0×10^{-9}	5.0×10^{-8}
Response time, s	10 - 15	–	–	10 - 15
Interfering ions $K^{pot}_{oxa,A^-} > 1.0 \times 10^{-2}$	–	SO_4^{2-}, PO_4^{3-}	SO_4^{2-}, PO_4^{3-}	ClO_4^-

[a]Ionophore I and II are [Fe (*o*-phenanthroline)$_3$]$^{2+}$ and [Fe(neocuproin)$_3$]$^{2+}$ respectively.

and the results are given in Tables 5 and 6. The results indicate that the proposed electrode can be successfully employed for the determination of oxalate at normal concentrations in water samples. The quality of results was evaluated by performing a recovery test, spiking the water sample with standard oxalate solution.

Conclusion

New oxalate-selective membrane electrode has been prepared using N,N'-bis(salicylidene)-2,2-dimethylpropane-1, 3-diamine Ni(II). The electrode has been shown to have good operating characteristics (Nernstian response; reasonable detection limit; relatively high selectivity, especially with respect to the highly lipophilic anions; wide dynamic range; fast response; applicability over a wide pH range). These characteristics and the typical applications presented in this paper, make the electrode suitable for measuring the oxalate content in water samples, without a significant interaction from concomitant anionic species. The results show that there was a coordination interaction between oxalate and the proposed carrier, which played an important role in the response characteristics and selectivity of the electrodes.

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